

# Steam reforming of ethanol over Pt/ceria with co-fed hydrogen

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## Abstract

Metal/ceria catalysts are receiving great interest for reactions involving steam conversion, including CO for low-temperature water–gas shift, and the conversion of chemical carriers of hydrogen, among them methanol, and ethanol. The mechanism by which ROH model reagents are activated on the surface of the Pt/partially reduced ceria catalyst was explored using a combination of reaction testing and infrared spectroscopy. In this particular investigation, the activation and turnover of ethanol were explored and compared with previous investigations of methanol steam reforming and low-temperature water–gas shift under H<sub>2</sub>-rich conditions, where the surface of ceria is in a partially reduced state. Under these conditions, activation of ethanol was found to proceed by dissociative adsorption at reduced defect sites on ceria (i.e., Ce surface atoms in the Ce<sup>3+</sup> oxidation state), yielding an adsorbed type II ethoxy species and an adsorbed H species, the latter identified to be a type II bridging OH group. In the presence of steam, the ethoxy species rapidly undergoes molecular transformation to an adsorbed acetate intermediate by oxidative dehydrogenation. This is analogous to the conversion of type II methoxy species to formate observed in previous investigations of methanol steam reforming. In addition, although formate then decomposes in steam to CO<sub>2</sub> and H<sub>2</sub> during methanol steam reforming, in an analogous pathway for ethanol steam reforming, the acetate intermediate decomposes in steam to CO<sub>2</sub> and CH<sub>4</sub>. Therefore, further H<sub>2</sub> production requires energy-intensive activation of CH<sub>4</sub>, which is not required for methanol conversion over Pt/ceria.

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**Keywords:** Cerium oxide; CeO<sub>2</sub>; Platinum; Pt; Hydrogen; H<sub>2</sub>; Steam reforming; Ethanol; Acetic acid; Methanol; Formate; Methoxy; Methoxide; Ethoxy; Ethoxide; Acetate; Fuel cell; Water–gas shift

## 1. Introduction

The main drivers that will determine the possibility of a hydrogen-based economy will be the achievement of key breakthroughs, cost reductions at all stages of development, and, certainly, government policies [1]. Infrastructure options for producing and delivering hydrogen currently under consideration include, among other competing technologies (e.g., hydrogen pipelines, cryogenic storage of hydrogen, metal-hydrides), the central production of high-energy density carriers, like methanol and ethanol, transport to a point of use, and reforming to release the hydrogen for fuel cell applications [2]. In terms of fuel flexibility, methanol has a distinct advantage over ethanol in that it can be produced from either CO and H<sub>2</sub> or CO<sub>2</sub> and H<sub>2</sub>, syngas sources that can be derived from the steam reform-

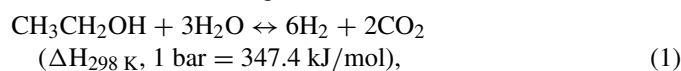
ing of hydrocarbons or gasification of coal and biomass. In the future, it is conceivable that methanol also could be produced from atmospheric CO<sub>2</sub> and H<sub>2</sub> generated by electrolysis using nuclear energy, as pointed out by Olah [3]. Ethanol, on the other hand, is receiving interest as a bio-fuel produced from the fermentation of corn and other renewable resources [4–6].

However, from the standpoint of steam-reforming catalysis, as a chemical carrier for hydrogen, methanol may offer other advantages, as highlighted in this work. Probably the two most important catalyst systems for hydrogen production applications include the M/ZnO (M = Cu, Pd) and M/CeO<sub>2</sub> systems, typically promoted by Pt, Pd, or other metals [7,8]. As seen in a review of the literature, these catalysts are used extensively in applications including conventional, oxidative, and autothermal steam reforming of alcohols like methanol (M/ZnO [9–38], M/CeO<sub>2</sub> [39–45]) or ethanol (M/ZnO [46–51], M/CeO<sub>2</sub> [52–57]), water–gas shift, and preferential oxidation of CO. The latter two reactions require a vast citation index, as detailed in some general reviews [7,8].

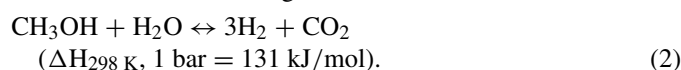
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The aims of the current investigation are to gain insight into the mechanism operating for the steam reforming of ethanol reaction over a Pt/ceria catalyst under hydrogen-containing conditions, and also to compare the findings with proposed mechanisms for related reactions, including water–gas shift and methanol steam reforming. That is, it is the goal of this work to assess how ethanol, as a model compound of the type ROH, is activated and turns over on sites consisting of partially reduced ceria in close proximity to Pt metal clusters. The ideal stoichiometry for hydrogen production from alcohol steam reforming is as follows:

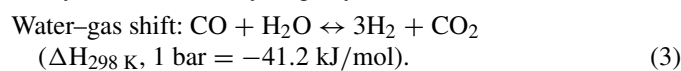
Ethanol steam reforming:



Methanol steam reforming:



It is also well known that the water–gas shift reaction significantly influences the hydrogen yield,



The method of comparing the reactivity of families of model compounds (e.g., ROH) has been extensively applied in the past. For example, Hutchings et al. [58] used the technique to probe the water–gas shift mechanism over Co and Cu/MnO catalysts. They reported that the key difference between a water–gas shift mechanism involving O adatoms (which may arise from hydroxyl group decomposition) in a regenerative (i.e., redox) process and one involving hydroxyl groups via a formate-type intermediate lies in how the water molecule decomposes on the surface. To probe the process on Cu/MnO, they used model molecules related to the H<sub>2</sub>O molecule, including CH<sub>3</sub>OH and CH<sub>3</sub>CH<sub>2</sub>OH. They concluded that methanol dissociates to give a methoxy intermediate and adsorbed H. They observed an analogous mechanism for ethanol dissociation. This result strongly suggests that water dissociates to give OH and H on the surface, and that the water–gas shift mechanism likely proceeds via an associative mechanism.

In 2005, Rioche et al. [59] examined the steam reforming of model compounds in relation to the steam reforming of bio-oil produced from biomass pyrolysis. They reported an important support effect with the addition of ceria–zirconia promoter to the catalyst over alumina alone during the conversion of acetic acid, acetone, ethanol, and phenol. The Pt/ceria–zirconia catalyst exhibited relatively good stability during a 9-h test, but temperatures above 800 °C were needed to achieve high yields of hydrogen and carbon oxides (i.e., CO, CO<sub>2</sub>) from ethanol, considerably higher than the reforming temperatures (400–500 °C) required to achieve significant conversion of methanol, which we reported that same year over Pt/ceria [44].

To probe the mechanism by which ethanol is activated and converts over Pt/ceria, we used a combination of in situ DRIFTS spectroscopy and fixed-bed reaction tests. Finally, we contrast the reformability of ethanol with our previous findings for methanol steam reforming from a mechanistic perspective.

## 2. Experimental

### 2.1. Catalyst preparation

Ceria with high surface area (~110 m<sup>2</sup>/g) was prepared by homogeneous precipitation of cerium nitrate using urea to slowly release the precipitating agent, the hydroxide anion. The resulting cerium hydroxide material was calcined at 400 °C for 4 h to produce nanoscale crystallites of CeO<sub>2</sub>. To load the platinum, ceria was impregnated with an aqueous solution of tetraammine platinum (II) nitrate, and the catalyst was aged overnight at room temperature, dried in a muffle furnace at 110 °C for 8 h, and recalced at 350 °C for 4 h, to decompose the platinum precursor. Details of the procedure are provided elsewhere [60], and background for the method has been given by Li et al. [61].

### 2.2. BET surface area

BET surface area measurements on the ceria and Pt/ceria materials were conducted using a Micromeritics Tristar 3000 gas adsorption analyzer. Approximately 250 mg of catalyst was used in each trial. A full 70-point isotherm was obtained at the boiling temperature of N<sub>2</sub> using N<sub>2</sub> as the adsorbate.

### 2.3. Catalyst activation

Activation of the ceria and Pt/ceria catalysts in hydrogen was followed by (1) temperature-programmed reduction (TPR), (2) X-ray absorption near-edge spectroscopy (XANES), and (3) diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Details of these procedures were provided previously [60]; a brief description is given here. TPR was conducted using a Zeton-Altamira AMI-200 unit, equipped with a thermal conductivity detector (TCD). Argon served as the reference gas, and 10% H<sub>2</sub> (balance Ar) was flowed at 30 cm<sup>3</sup>/min as the temperature was increased from 50 to 1100 °C. XANES was carried out using a fabricated in situ flow cell at the Ce L<sub>III</sub> (5723 eV) edge at beamline X18b, Brookhaven National Laboratory, Upton, New York. Smooth self-supporting, pinhole-free pellets were pressed and loaded into the cell, and the treatment gas (H<sub>2</sub>) was directed directly at the sample area. Scans were obtained in transmission mode as the cell temperature was raised in 50 °C increments. Partial reduction of ceria was observed to occur at ~250 °C. Linear combination XANES fits of treated catalysts with reference standards were carried out using WinXAS [62].

### 2.4. DRIFTS

DRIFTS spectra were obtained using a Nicolet Nexus 870 spectroscope equipped with a DTGS-TEC detector. A high-pressure/high-temperature cell fitted with ZnSe windows (Thermo Spectra-tech) served as the reaction chamber for in situ adsorption and reaction measurements. The gas lines leading to and from the reactor were heat-traced to prevent condensation and were also covered with ceramic fiber tape and insulating

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